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NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
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in its capacity as elected Office

Date of mailing (day/month/year) 06 February 2001 (06.02.01)	
International application No. PCT/AU00/00696	Applicant's or agent's file reference fp12892
International filing date (day/month/year) 20 June 2000 (20.06.00)	Priority date (day/month/year) 22 June 1999 (22.06.99)
Applicant TRAN, Nguyen, Hoang et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

05 January 2001 (05.01.01)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

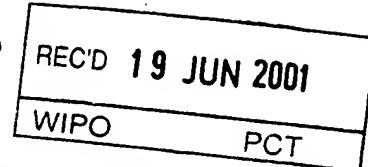
The International Bureau of WIPO 34, chemin des Colombettes 1211 Genève 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer R. E. Stoffel Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



14

Applicant's or agent's file reference AJM:MG:FP12892	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).	
International Application No. PCT/AU00/00696	International Filing Date (day/month/year) 20 June 2000	Priority Date (day/month/year) 22 June 1999
International Patent Classification (IPC) or national classification and IPC Int. Cl.⁷ C30B 25/02, 29/48, H01L 21/365		
Applicant UNISEARCH LIMITED et al		

1.	This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.																
2.	<p>This REPORT consists of a total of 3 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 4 sheet(s).</p>																
3.	<p>This report contains indications relating to the following items:</p> <table border="0"> <tr> <td>I</td> <td><input checked="" type="checkbox"/> Basis of the report</td> </tr> <tr> <td>II</td> <td><input type="checkbox"/> Priority</td> </tr> <tr> <td>III</td> <td><input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td>IV</td> <td><input type="checkbox"/> Lack of unity of invention</td> </tr> <tr> <td>V</td> <td><input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td>VI</td> <td><input type="checkbox"/> Certain documents cited</td> </tr> <tr> <td>VII</td> <td><input type="checkbox"/> Certain defects in the international application</td> </tr> <tr> <td>VIII</td> <td><input type="checkbox"/> Certain observations on the international application</td> </tr> </table>	I	<input checked="" type="checkbox"/> Basis of the report	II	<input type="checkbox"/> Priority	III	<input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	IV	<input type="checkbox"/> Lack of unity of invention	V	<input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	VI	<input type="checkbox"/> Certain documents cited	VII	<input type="checkbox"/> Certain defects in the international application	VIII	<input type="checkbox"/> Certain observations on the international application
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VI	<input type="checkbox"/> Certain documents cited																
VII	<input type="checkbox"/> Certain defects in the international application																
VIII	<input type="checkbox"/> Certain observations on the international application																

Date of submission of the demand 5 January 2001	Date of completion of the report 7 June 2001
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer R.P. ALLEN Telephone No. (02) 6283 2134

I. Basis of the report

1. With regard to the **elements** of the international application:*
- ☐ the international application as originally filed.
- ☒ the description, pages **1, 4-9** , as originally filed,
pages , filed with the demand,
pages **2-3** , received on **29 May 2001** with the letter of **28 May 2001**
- ☒ the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages **10-11** , received on **29 May 2001** with the letter of **28 May 2001**
- ☒ the drawings, pages **1-8** , as originally filed,
pages , filed with the demand,
pages , received on with the letter of
- ☐ the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of
2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:
- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
4. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Claims 1-17	YES
	Claims	NO
Inventive step (IS)	Claims 1-17	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-17	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)Citations

- (a) Metalloorganicheskaia Khimiia, 1, No.3, 1988 (Druz et al.) "Growth Epitaxial Films of Sulfides of Cadmium and Zinc from Dithiocarbamate Compounds $M(S_2CNET_2)_2$ ($M=Cd, Zn$)", see pages 645 - 649.
- (b) Thin Solid Films, 271, 1995 (Nomura et al.) "Single-Source MOVPE Growth of Zinc Sulfide Thin Films Using Zinc Dithiocarbamate Compexes", see pages 4-7.
- (c) Journal Of The American Chemical Society, 119, No.16, 23 April 1997 (Cheon et al.) "Gas Phase Photochemical Synthesis Of II/VI Metal Sulfide Films...", see pages 3838-3839.
- (d) Journal of Crystal Growth, 97, 1989 (Jones et al.) "The Growth of CdS and CdSe Alloys by MOCVD using a New Dimethylcadmium Adduct" see pages 537-541
- (e) Derwent Abstract Accession No. 96-496203/49, Class E12, RU 2055948 C1,(AS SIBE INORG CHEM INST) 10 March 1996
- (f) Patent Abstract of Japan, JP 11087747 A (MATSUSHITA DENCHI KOGYO KK) 30 March 1999 & JP 11087747 A

Novelty & Inventive Step

Claim 1-17 None of the citations, or obvious combination thereof, disclose all of the features of any of these claims. The claims are limited to epitaxial zinc-based II-IV semiconductor films. Although citation (a) discloses single source process for growth of epitaxial ZnS films the applicant asserts that these attempts were unsuccessful. It is argued that the results indicated the formation of polycrystalline ZnS films. Citation (a) does however disclose epitaxial CdS films.

(19) World Intellectual Property Organization
International Bureau



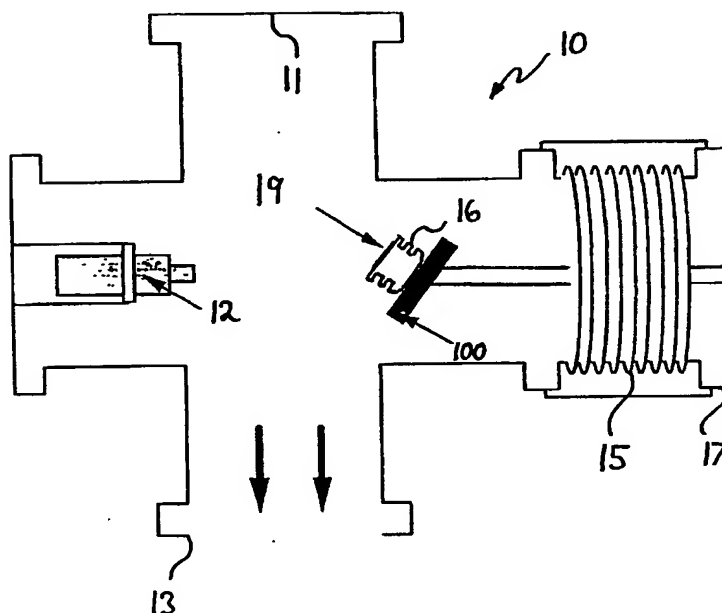
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- (71) Applicant (for all designated States except US):
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- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
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- (75) Inventors/Applicants (for US only): TRAN, Nguyen, Hoang [AU/AU]; 22 Bent Street, Altona, VIC 3018 (AU). HARTMANN, Andreas, Jorgen [DE/AU]; 45 Newman Street, Newtown, NSW 2042 (AU). LAMB, Robert, Norman [AU/AU]; 9 Gamut Road, Engadine, NSW 2233 (AU).
- Published:
— With international search report.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: EPITAXIAL FILMS



Applicants
PCT

WO 00/79033 A1

(57) Abstract: Growth of epitaxial zinc sulphide semiconductor film using zinc diethyldithiocarbamate precursor as single source.

EPITAXIAL FILMSField of the Invention

The present invention relates broadly to the growth of epitaxial II-VI semiconductor films. The invention will be described herein with reference to the growth of epitaxial zinc sulfide (ZnS) on silicon (Si) (111) substrates, but it will be appreciated that the invention does have broader applications relating to growth of epitaxial II-VI semiconductor films of different materials and/or on different substrates.

Background of the Invention

Films that grow with singular crystallographic orientation in all directions are referred to as epitaxial films. This has to be contrasted with poly-crystalline thin films, which include a large number of crystallites — but with variable orientations with respect to each other.

Epitaxial thin films have been produced using a variety of different techniques, including molecular beam epitaxy (MBE), vapour phase epitaxy (VPE) and atomic layer epitaxy (ALE). However, a common characteristic of those techniques is that the epitaxial film growth requires multiple sources for the film elements, for example separate sources for zinc (Zn) and sulphur (S) are required for the epitaxial growth of ZnS films. Therefore, such techniques can have the disadvantage of being rather complex processes, during which a large number of variables must be controlled. This often results in high costs associated with the operation of machines for epitaxial film growth.

Epitaxial thin films are desirable for a large number of applications including light emitting layers for diodes, as active layers in optical/electro-optical thin film devices and as coatings. In this application, the single-crystal like characteristics of epitaxial films are utilised, which are typically superior to the characteristics of polycrystalline films.

Summary of the Invention

In accordance with a first aspect of the present invention there is provided an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

In one embodiment, the epitaxial film comprises ZnS. Preferably, the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $\text{Zn}(\text{S}_2\text{CNR}_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

In accordance with a second aspect of the present invention there is provided a process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial II-VI semiconductor film on a substrate.

In one embodiment, the epitaxial film comprises ZnS.

In one preferred embodiment the process comprises the use of zinc diethyldithiocarbamate as a precursor for the single source chemical vapour deposition.

In another preferred embodiment, the ZnS is grown using $\text{Nz}(\text{S}_2\text{CNR}_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

The number of carbon atoms in the alkyl group is preferably in the range from 1 to 6.

Preferably, the substrate comprises a silicon (111) substrate.

In accordance with a third aspect of the present invention, there is provided a substrate coated with a coating comprising an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS.

In accordance with a fourth aspect of the present invention, there is provided a process for growing an epitaxial II-VI semiconductor film, the process comprising the steps of cleaning a substrate, heating the substrate to
5 a deposition temperature, the sublimation of a single source chemical vapour deposition precursor;

the pyrolysis of the precursor molecules on the heated substrate; and

the formation of the epitaxial film on the heated
10 substrate.

Preferably, the substrate comprises silicon (111).

In one embodiment, the epitaxial film comprises ZnS.

Preferred forms of the invention will now be described, by way of example only, with reference to the
15 accompanying drawings.

Brief Description of the Drawings

Figure 1 is a schematic drawing of a deposition chamber embodying the present invention.

Figure 2 shows angle dependent X-ray photoelectron
20 defraction measurements of epitaxial films embodying the present invention.

Figure 3 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 4 shows an X-ray photoelectron spectroscopy
25 wide scan of a ZnS film embodying the present invention.

Figure 5 shows an angle dependent X-ray photoelectron defraction measurements of a ZnS film after sputtering.

Figure 6 shows energy dependent X-ray photoelectron defraction measurements of an epitaxial film embodying the
30 present invention.

Figure 7 is schematic drawing illustrating a side view of a ZnS crystalline structure.

Figure 8 is a schematic drawing illustrating the formation of an epitaxial film embodying the present
35 invention.

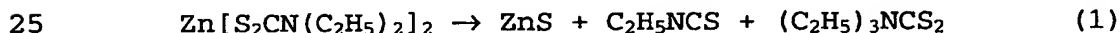
Figure 9 is a block diagram illustrating the growth of epitaxial films embodying the present invention.

Figure 10 is a schematic diagram illustrating a device application embodying the present invention.

5 Detailed Description of the Preferred Embodiments

In Figure 1, a high vacuum deposition chamber 10 (base pressure 10^{-7} Torr) comprises a resistively heated Knudsen cell 12 loaded with a zinc diethyldithiocarbamate precursor powder (not shown) for the single source chemical vapour
10 deposition (SSCVD). A silicon Si(111) substrate 19 is mounted on a sample holder 16 on a heater 100 and the epitaxial film (not shown) is formed on the substrate 19. The chamber 10 further comprises a view port 11, a port 13 to which a vacuum pump (not shown) is connected and a
15 flexible flange 15 as part of a x,y,z manipulator 17 for the heater 100.

As illustrated in Figure 8, sublimed zinc diethyldithiocarbamate molecules 80 impinge on the heated substrate 19. In the diethyldithiocarbamate molecules 80,
20 the zinc atom is in a similar environment to that of zinc in crystalline ZnS. The SSCVD growth of the ZnS epitaxial film 84 proceeds via the pyrolysis of $\text{Zn}[\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2]_2$ on the heated substrate 19 (400°C):



$\text{C}_2\text{H}_5\text{NCS}$ and $(\text{C}_2\text{H}_5)_3\text{NCS}_2$ decompose into by-products such as C_2H_4 , CS_2 and $(\text{C}_2\text{H}_5)\text{NH}$ which are volatile in vacuum and therefore do not remain on the heated substrate 19 during
30 the ZnS epitaxial film growth.

In this embodiment epitaxial film growth of ZnS was found on the Si (111) surface (lattice mismatch $\sim 0.2\%$).

As shown in Figure 9, in one embodiment the growth of epitaxial films comprises the cleaning of the Si substrate
35 (step 90), the heating of the Si substrate (step 92), the sublimation of the diethyldithiocarbamate precursor (step

94), the pyrolysis of the diethyldithiocarbamate molecules on the heated substrate (step 96) and the formation of the epitaxial ZnS film on the heated substrate (step 98).

The cleaning of the Si(111) substrates (step 90) in one embodiment comprises the sequence of steps outlined in Table 1.

1	annealing in oxygen	1050°C	30 min
2	rinse in deionised H ₂ O	room temp	5 min
	(ultrasonic bath)		
3	rinse in EtOH	room temp	5 min
	(ultrasonic bath)		
4	rinse in Iso-propyl alcohol	room temp	5 min
	(ultrasonic bath)		
5	N ₂ blown dry		30 sec
6	12H ₂ O : 7NHF ₄ : 1HF	room temp	10 min
7	rinse in deionised H ₂ O	room temp	1 min
8	N ₂ blown dry		30 sec
9	5H ₂ O : 1HCl : 1H ₂ O ₂	80°C, oil bath	10 min
10	rinse in deionised H ₂ O	room temp	1 min
11	N ₂ blown dry		30 sec
12	12H ₂ O : 7NHF ₄ : 1HF	room temp	10 min
13	rinse in deionised H ₂ O	room temp	1 min
14	N ₂ blown dry		30 sec
15	5H ₂ O : 1HCl : 1H ₂ O ₂	80°C, oil bath	10 min
16	rinse in deionised H ₂ O	room temp	1 min
17	N ₂ blown dry		30 sec
18	12H ₂ O : 7NHF ₄ : 1HF	room temp	10 min
19	rinse in deionised H ₂ O	room temp	1 min
20	N ₂ blown dry		30 sec
21	5H ₂ O : 1HCl : 1H ₂ O ₂	80°C, oil bath	10 min
22	rinse in deionised H ₂ O	room temp	1 min
23	N ₂ blown dry		30 sec
24	NH ₄ F (40%) or HF (5%)	room temp	10 min

25	rinse in absolute EtOH room temp	2 min
26	Mounting onto sample holder/heater	16
27	loading into deposition chamber	10
28	heating for removing surface contaminants	350°C, vacuum (10^{-8} torr)
		1 5 m i n

In will be appreciated, however, that other cleaning step sequences and different treatment times may be applied, which may e.g. comprise sputtering and annealing steps in the high vacuum deposition chamber 10 (Figure 1).

Film Characterisation

The resulting epitaxial films were characterised using X-ray photoelectron spectroscopy (XPS) and X-ray photoelectron diffraction (XPD).

Figure 2 shows an angle dependent XPD scan of the Zn $2p_{3/2}$ intensity distribution for ZnS epitaxial films at thicknesses ranging from ~5 to 2000Å. The film thicknesses were estimated using the intensity attenuating of the XPS Si substrate peaks. The XPD measurements were performed after subsequent SSCVD deposition cycles.

The XPD patterns exhibit an intense and broad peaks 20, 22, and 24 at $\theta=0^\circ$ which are the result of forward-scattering of Zn $2p_{3/2}$ photoelectrons by neighbouring atoms. In ZnS, every zinc atom is surrounded by four sulfur atoms in a tetrahedral arrangement which results in either a cubic (sphalerite) or a, slightly distorted, hexagonal (wurtzite) structure.

The enhanced XPD intensities 20, 22, 24 at $\theta=0^\circ$ in curves a, b, and c of Figure 2 respectively therefore indicate that the film molecules have preferred orientation at the film-to-substrate interface and the Zn $2p_{3/2}$ photoelectrons are scattered by the sulfur neighbours perpendicular to the substrate.

As illustrated in Figure 3, the forward scattering enhancement 20, 22, 24 at $\theta=0^\circ$ in curves a, b and c of Figure 2 is likely the result of forward-scattering of Zn $2p_{3/2}$ photoelectrons emitted from the zinc atoms 30 at the sulphur atoms 32, which are positioned directly above the zinc atoms 30 at a distance of 2.3 Å in an ideal ZnS cubic crystal structure.

In Figure 4, a XPS wide scan 40 for a typical ZnS epitaxial film embodying the present invention is shown. In the curve 40 shown in Figure 4, the silicon substrate peaks can also be observed, which are not fully attenuated due to the thinness of the ZnS epitaxial film on which the XPS measurement shown in Figure 4 was performed. The chemical composition obtained from XPS scans such as the one shown in Figure 4 were in agreement with those obtained for a ZnS reference sample.

In Figure 5, the curve 50 shows the XPD measurement for the 2000Å thick film of curve c of Figure 2 after Ar⁺ ion etching.

During the Ar⁺ ion etching, highly energetic (2000 electron Volt (2keV)) impact on the film surface, resulting in a disordering of the crystallographic structure of the surface. In curve 50 of Figure 5, the XPD scan therefore does not indicate a significant forward scattering enhancement at $\theta=0^\circ$.

Energy dependent XPD was employed to probe the in-plane orientation of the film molecules. The sample position and angle remained unchanged while the energy of the incoming X-rays was varied.

The energy dependent XPD features shown in Figure 6 are a result of diffraction of S 2p photoelectrons in the ZnS atomic network. The photoelectron take-off angle was 19° with respect to the surface plane, i.e. the measurement was sensitive for crystallographic order within the plane of the substrate. As diffraction is a long range order process (diffraction of photoelectrons requires single crystalline surfaces) the observation of peaks 60, 62, 64 demonstrates that the film is of epitaxial quality.

As illustrated in Figure 7, the peaks 60, 62, 64 in the measurement shown in Figure 6 are due to the forward scattering of S 2p photoelectrons emitted from the sulphur atoms 70 at zinc atoms 72, which are the next neighbours of the sulphur atoms 70 in the $[11\bar{1}]$ crystallographic direction 74, along which the measurement shown in Figure 6 was measured. The distance between the sulfur atoms 60 and the Zn atoms 72 in an ideal ZnS cubic crystal structure is 2.3 Å.

In the following, a specific device application embodying the present invention will be described with reference to Figure 10.

Silicon is transparent at the typical telecommunications wavelength and it has been shown that Silicon-On-Insulator (SOI) structures can be used as waveguides. In these structures the wave is guided by a thin silicon layer on SiO₂.

Figure 10 illustrates the principles of an optical modulator design 100. The silicon 102 is partially replaced by an epitaxial ZnS layer 104 which acts as waveguide. A suitable AC voltage applied across the ZnS layer 104 alters the refractive index of the ZnS and it is therefore possible to modulate light 105 guided through the film directly.

The epitaxial ZnS layer 104 is grown on the remaining slightly doped (111) oriented silicon layers 106 which also comprises the bottom electrode. A thin metal film 108

(e.g. Cr) is deposited onto the ZnS film 104 and form the top electrode. Optical losses are dependent on the density of defects in the ZnS layer 104 and it is therefore of significant advantage that they can be grown single

5 crystalline using the technology of the present invention.

It will be appreciated by a person skilled in the art that the present invention is not limited to that specific application, but other applications are possible, including for example in other optical modulator devices, optical
10 waveguide devices, transistor and diode devices, blue light emitting devices, solar cells, and as coatings for infrared sensing, emitting, or transmitting devices.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due
15 to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

In the claims that follow and in the summary of the invention, except where the context requires otherwise due
20 to express language or necessary implication, the word "comprising" is used in the sense of "including", i.e. the features specified may be associated with further features in various embodiments of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

2. An epitaxial film as claimed in claim 1, wherein
5 the epitaxial film comprises ZnS.

3. An epitaxial film as claimed in claim 2, wherein the ZnS is grown using zinc diethyldithiocarbamate as precursor for the single source chemical vapour deposition.

4. An epitaxial film as claimed in claim 2, wherein
10 the ZnS is grown using $\text{Zn}(\text{S}_2\text{CNR}_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

5. A process as claimed in claim 4, wherein the number of carbon atoms in the alkyl group is in the range
15 from 1 to 6.

6. A process comprising the steps of utilising single source chemical vapour deposition for growing an epitaxial II-VI semiconductor film on a substrate.

7. A process as claimed in claim 6, wherein the
20 epitaxial film comprises ZnS.

8. A process as claimed in claim 7, wherein the process comprises the use of $\text{Zn}(\text{S}_2\text{CNR}_2)_2$, where R comprises an alkyl group, as a precursor for the single source chemical vapour deposition.

25 9. A process as claimed in claim 8, wherein the number of carbon atoms in the alkyl group is in the range from 1 to 6.

10. A process as claimed in claim 7, wherein the process comprises the use of zinc diethyldithiocarbamate as
30 a precursor for the single source chemical vapour deposition.

11. A process as claimed in any one of claims 6 to 10, wherein the substrate comprises a silicon (111) substrate.

12. A substrate coated with a coating comprising an epitaxial II-VI semiconductor film grown using single source chemical vapour deposition.

13. A substrate as claimed in claim 12, wherein the
5 substrate comprises silicon (111).

14. A substrate as claimed in claims 12 or 13, wherein the epitaxial film comprises ZnS.

15. A process for growing an epitaxial II-VI semiconductor film, the process comprising the steps of:

- 10 - cleaning a substrate,
 - heating the substrate to a deposition temperature,
 - the sublimation of a single source chemical vapour deposition precursor;
 - the pyrolysis of the precursor molecules on the
15 heated substrate; and
 - the formation of the epitaxial film on the heated substrate.

16. A process as claimed in claim 15, wherein the substrate comprises silicon (111).

20 17. A process as claimed in claim 15 or 16, wherein the epitaxial film comprises ZnS.

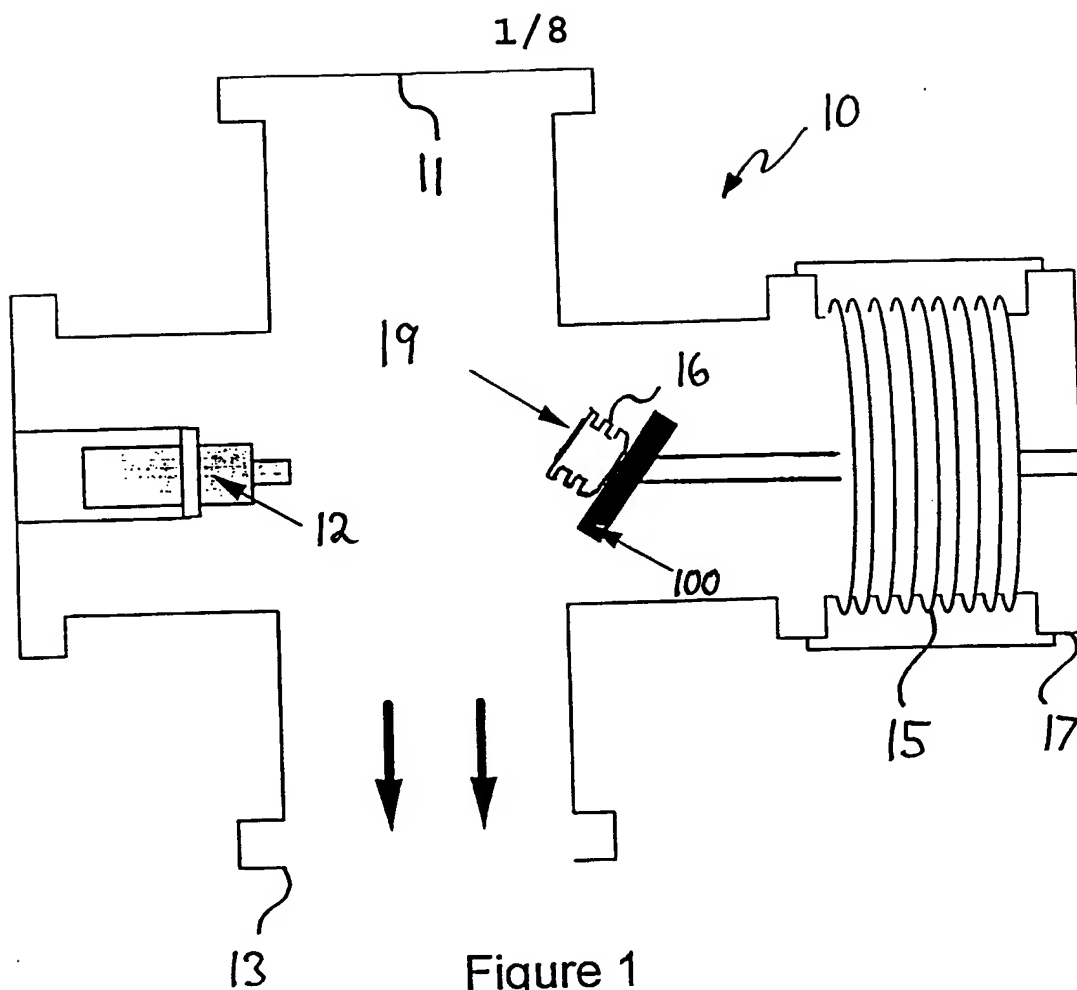


Figure 1

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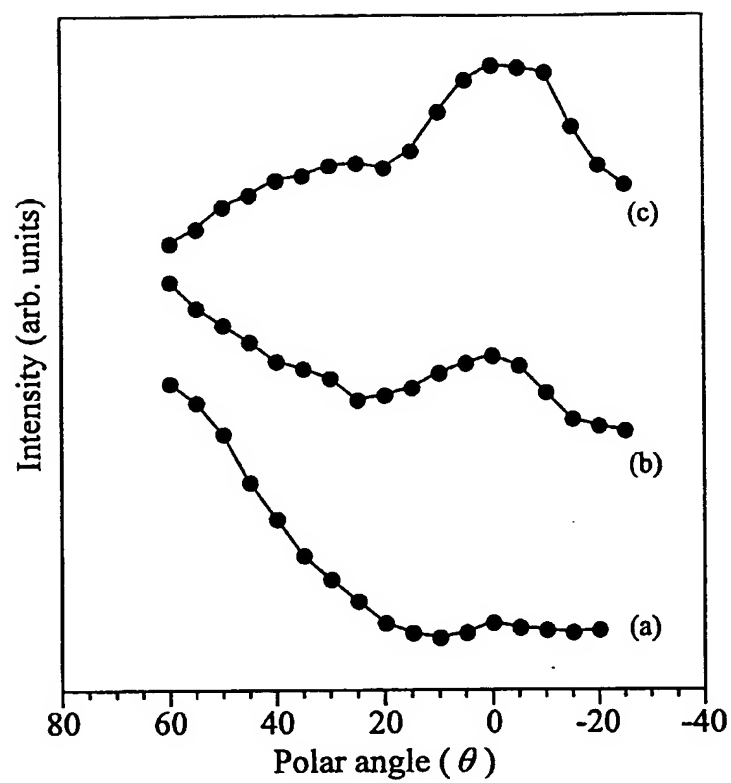


Figure 2

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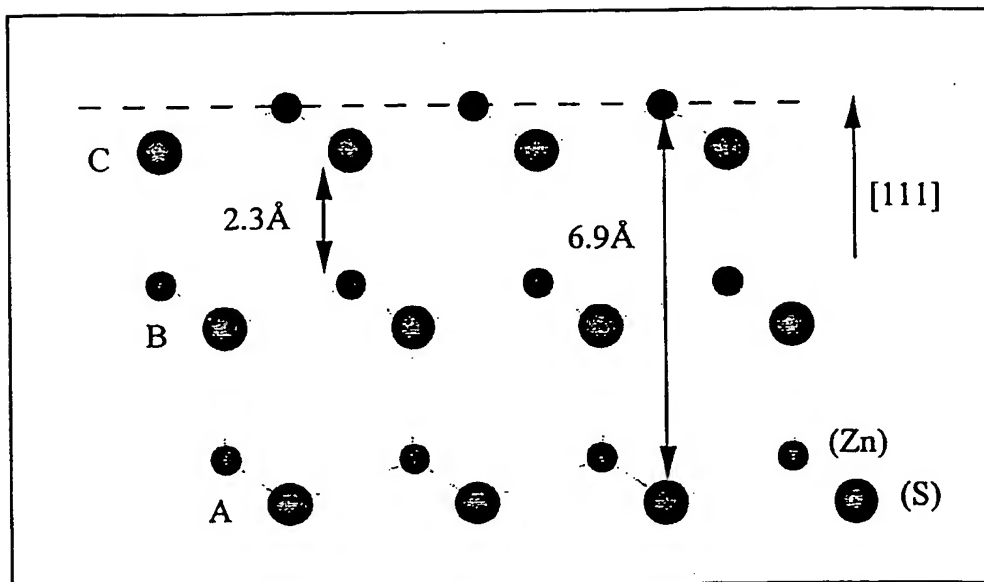


Figure 3

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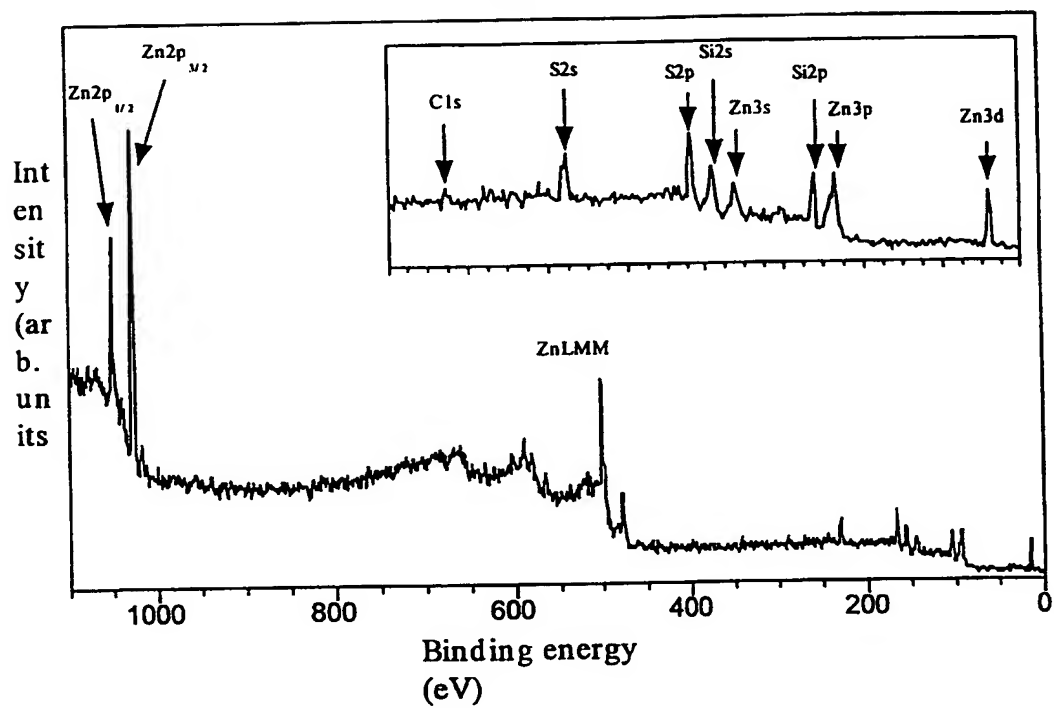


Figure 4

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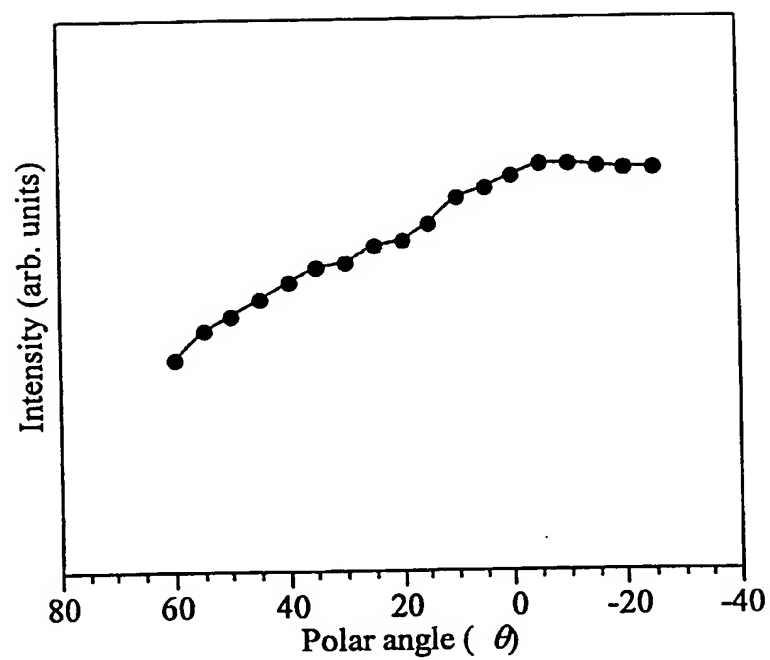


Figure 5

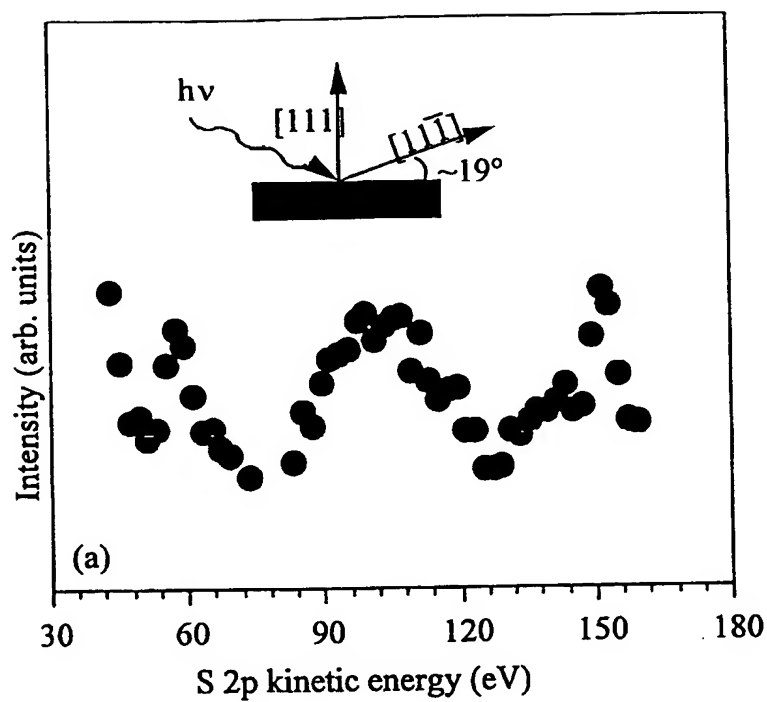


Figure 6

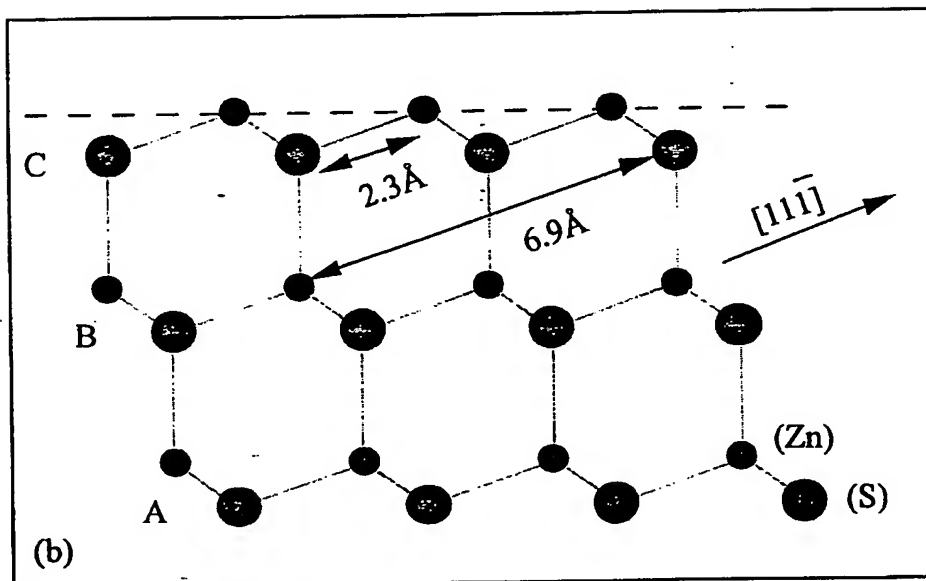


Figure 7

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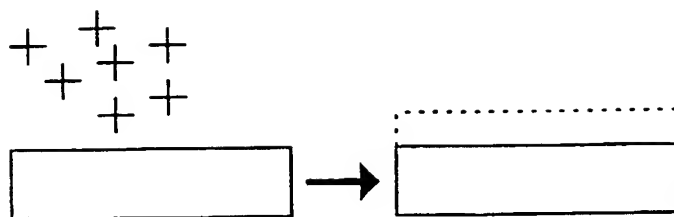


Figure 8

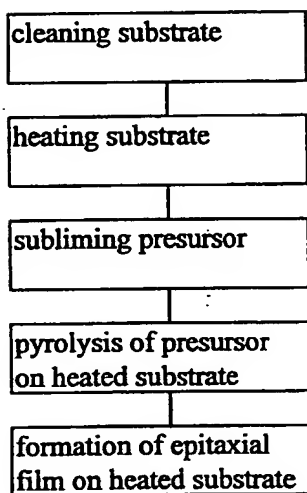


Figure 9

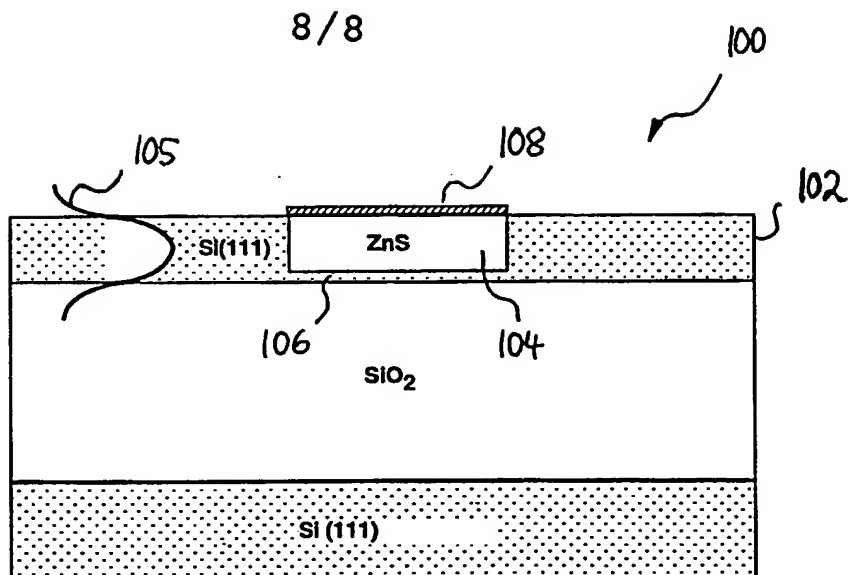


Figure 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00696

A. CLASSIFICATION OF SUBJECT MATTER	
Int. Cl. ⁷ : C30B 25/02, 29/48, H01L 21/365	
According to International Patent Classification (IPC) or to both national classification and IPC	
B. FIELDS SEARCHED	
Minimum documentation searched (classification system followed by classification symbols) C30B 25/02, 29/48, C23C 16/30, H01L 21/365	
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched	
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) dwpi IPC and (singl+ or vapo+) and (source+ or precurs+) caplus dithiocarbamate and zinc and semiconductor	
C. DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages
X	Metalloorganicheskaia Khimiia, 1, No.3, 1988 (Druz et al.) "Growth Epitaxial Films of Sulfides of Cadmium and Zinc from Dithiocarbamate Compounds $M(S_2CNEt_2)_2$ ($M=Cd, Zn$)", see pages 645 - 649.
X	Thin Solid Films, 271, 1995 (Nomura et al.) "Single-Source MOVPE Growth of Zinc Sulfide Thin Films Using Zinc Dithiocarbamate Complexes", see pages 4-7.
X	Journal Of The American Chemical Society, 119, No.16, 23 April 1997 (Cheon et al.) "Gas Phase Photochemical Synthesis Of II/VI Metal Sulfide Films...", see pages 3838-3839.
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex	
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
Date of the actual completion of the international search 9 August 2000	Date of mailing of the international search report 22 AUG 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929	Authorized officer R.P. ALLEN Telephone No : (02) 6283 2134

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/00696

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Journal of Crystal Growth, 97, 1989 (Jones et al.) "The Growth of CdS and CdSe Alloys by MOCVD using a New Dimethylcadmium Adduct" see pages 537-541	1
X	Derwent Abstract Accession No. 96-496203/49, Class E12, RU 2055948 C1,(AS SIBE INORG CHEM INST) 10 March 1996	1, 15-16
X	Patent Abstract of Japan, JP 11087747 A (MATSUSHITA DENCHI KOGYO KK) 30 March 1999 & JP 11087747 A	1-17

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00696

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member
JP	11087747	NONE	
RU	2055948	NONE	
			END OF ANNEX